

Keratin Coatings for Wool: Shrinkproofing and Nanoparticle Delivery

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Summary: Wool fabrics were treated with keratin hydrolysate in isolated systems, in systems incorporating a cross-linking enzyme, and in systems with nanoparticle silver. The dimensions of wool fabric were controlled after keratin applications and the strength of bleached wool fabric was improved. Keratin applications imparted these improved properties when applied alone and when applied with the enzyme. The enzyme was effective for in-situ, solid-state cross-linking of wool fabric, cross-linking keratin-to-keratin, and cross-linking keratin-to-fabric. To further improve the properties of wool, nanoparticle silver was produced in various shapes. Transmission electron microscopy (TEM) micrographs of these particles showed discrete and isolated particles of size 8–100 nm, dependent on the preparation. A combination of TEM and UV-VIS spectroscopy was used to characterize these particles and scanning electron microscopy running in backscattered electron mode confirmed their placement on wool fibers. The application of nanoparticle silver to wool when co-added with keratin may both improve dimensional stability and impart antimicrobial efficacy.

Keywords: enzyme; keratin; nanoparticle; silver; wool

Introduction

Enzyme treatments are applied to wool to impart dimensional stability without strength loss as an alternative to chlorination, which is known to be ecologically hazardous. We have published a novel chemoenzymatic process (ARS Process). The process, an alternative to chlorination, utilizes an in-situ formed, activated peroxide, peroxydicarboximide acid. This peroxide bleaching step whitens and primes the wool fiber cuticle for subsequent enzyme digestion, which selectively smoothes the surface scales of the cuticle to biopolish and shrinkproof wool.^[1] ARS machine-washable, itch-free wool exhibited up to 18% strength loss in fine jersey wool fabrics that could be compensated by changing to a different knit fabric construction and /or different choice

of fabric components such as yarn and knit gage. Nonetheless, we applied keratin hydrolysate obtained by dissolving wool to ARS-bleached wool in place of the enzyme step and observed shrinkage control without strength loss in these fabrics.^[2,3,4] Fabricated silver nanoparticles delivered to wool exhibited fiber adhesion after rinsing.

Morphology

Wool fibers (Figure 1a), composed of keratin polypeptide, gain structural integrity through an alpha helix configuration stabilized by cross-linked disulfide bonds of the amino acid cysteine. Ionized forms of free NH_2 and COOH groups of diamino and dicarboxyl amino acids combine to form salt linkages (polar bonds) with functionality important for metal ion chelation and nanoparticle adhesion to wool. Selective hydrophilic treatment of wool is hindered by the hydrophobic lipid layer on the fiber cuticle. The ARS process of bleaching removes this layer

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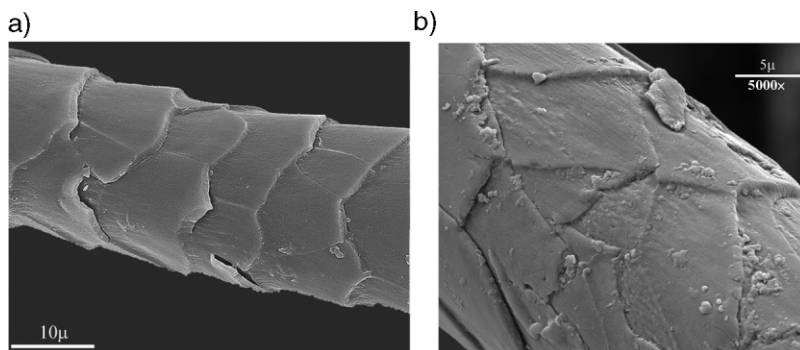


Figure 1.

a,b. Wool fiber: (a) untreated (b) treated with KP applied with microbial transglutaminase.

to predispose the fiber surface to treatment. Previous experiments have shown that keratin hydrolysate prepared by alkali treatment and lyophilized keratin hydrolysate (KP) exhibit strong adhesion to ARS bleached wool (Figure 1b).^[1]

As reported previously, when keratin hydrolysate was applied in the presence of microbial transglutaminase (mTgase) to wool fabric after ARS bleaching, dimensional stability of the fabric was controlled to less than 5% area shrinkage and fiber strength was improved (Figure 2).^[1,2,3] mTgase mediation provided *in-situ*, self-cross-linking of wool in its fibrous state, cross-linking of solubilized keratin to wool, and cross-linking of solubilized keratin to itself. Figure 2 illustrates the isolated and combined effects of KP and mTgase. Note that KP and mTgase alone control shrinkage, but the combined effect is greater.

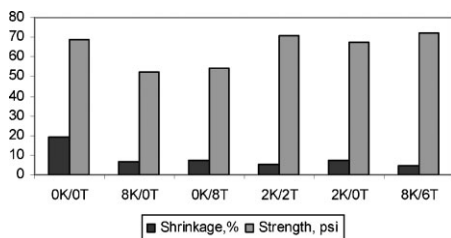


Figure 2.

Physical effects of treating ARS-bleached wool fabric with KP co-added with microbial transglutaminase. OK/OT is the untreated, control fabric; 8K/6T indicates that 8% on the weight of fabric (owf) KP was applied with 6% owf mTgase.

Note also that the combined effect of KP and mTgase has the greatest positive impact on fiber strength improvement.

Wool has chelating properties as exhibited in mordant dyeing with premordantized dyes.^[5-8] We became interested in exploiting the established affinity of wool and wool keratins toward transition metals in the development of the next generation fabrics that incorporate inorganic nanoparticles. To this end, we investigated the use of solubilized wool keratins to deliver silver nanoparticles to the wool fiber surface with mTgase.

Nanoparticle Applications of KP and mTgase to Wool

Jersey knit wool fabric (~20 μ) (TF 532; West Pittston, NJ) was used as a substrate for nanoparticle-enriched keratin treatments. Silver nitrate, sodium citrate and sodium borohydride were purchased from Aldrich and used as received. De-ionized water was obtained using a Barnstead Nanopure filtration system.

TEM images were recorded using a Phillips CM12 Cryo system. SEM images were recorded in low vacuum mode (water vapor), using an FEI Quanta 200F scope. UV-VIS measurements of the SPR band were recorded using a Cary 50 Conc spectrometer and a Tecan Microplate Reader equipped with XFluor4SafireII software v4.62A (100 averages).

Water-soluble keratin hydrolysate was prepared using a minor modification of a

previously published procedure.^[1] Colloidal silver nanoparticles (yellow) were prepared using a modification of a method previously reported by Mirkin *et al.*^[9] In a typical experiment, spherical silver nanoparticles were prepared by the dropwise addition of 1 mL 0.050 M sodium borohydride into a gently stirring solution of aqueous silver nitrate (0.1 mM, 100 mL) and trisodium citrate (0.3 mM). After stirring the mixture for several minutes, it was irradiated with white light using various configurations, which allowed us to generate a wide variety of primary colors corresponding to various shapes and sizes of silver nanoparticles.^[10] One such solution was used in the preparation of nanoparticle-treated keratin hydrolysate. To prepare this material, 1 g of keratin hydrolysate was dissolved in the minimum amount of nanoparticle solution needed to completely dissolve the hydrolysate. To ensure complete dissolution, the entire mixture was heated gently at approximately 50 °C under stirring for about ten minutes. The viscous solution was then poured onto an evaporating dish and was allowed to evaporate, forming a brittle thin film. This material was collected and used to prepare nanoparticle cross-linked fabrics using an approach outlined in previous publications.^[2,3] The fabrics were vigorously rinsed with deionized water and agitation prior to analysis.

Analysis of Nanoparticle KP and mTgase Treatment

Excitation of the colloid with visible light (350–700 nm) results in the photoinduced

conversion of silver nanoparticles into various structures. These structures are markedly unlike the spherical nature of the initial colloid and have been reported to form triangular nanoprisms and truncated triangular nanoprisms in excellent yield.^[9] Other polygons have also been observed with TEM using the reported method, but were not present in sufficiently high yields as the color of the colloids was dominated by the surface plasmon absorbance of triangular nanoprisms.^[9] The size and shape of nanocrystalline materials have important implications for many of the observed physical and chemical properties.^[11,12] Figure 3 demonstrates an assortment of colors that we have obtained from excitation of the spherical colloid using visible light using our method and published procedures.^[9] The physical and chemical characterization of these colloids and their application to wool are beyond the scope of this investigation and will be detailed in a future publication.^[10]

The purple colloid, shown far left in Figure 3, was chosen to prepare the keratin material used in this study due to its striking color, since we wanted to evaluate the potential to use these colloids as functional dyes. TEM analysis revealed high order polygonal structures, where the number of sides ranged from 4–8 for these nanoparticles, as well as the presence of a small amount of triangular nanoprisms and truncated triangular nanoprisms, shown in Figure 4. Further irradiation of the sample could not convert the triangular nanoparticles into high order polygons, and the



Figure 3.

Silver nanoparticle solutions prepared using a modification of the Mirkin method. Colors (left to right): purple, blue, green, yellow, orange.

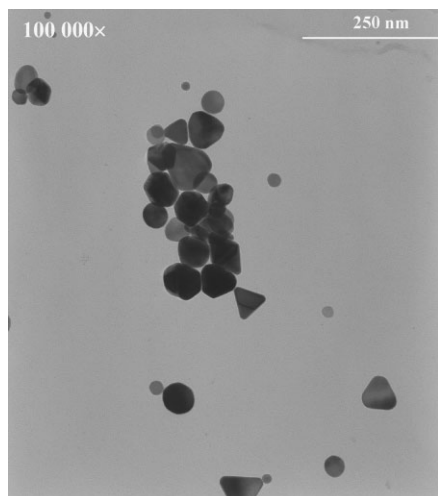


Figure 4.

Predominantly higher order polygonal nature of the purple colloid.

color did not change, suggesting that the triangular structures and the polygons are quite stable to photochemical conversion once formed.

SEM analysis in low vacuum mode was used to examine the structure of the treated fabrics without the need for metallic or conductive coatings. We utilized backscattered electrons, which scatter back from the sample as a function of atomic number, to identify domains rich with silver nanoparticles based on contrast differences (Figure 5). As this method cross-links keratin to the fabric surface and does not destroy the scalar structure of the fabric, the scalar component of the wool fiber is often observed in backscattered images

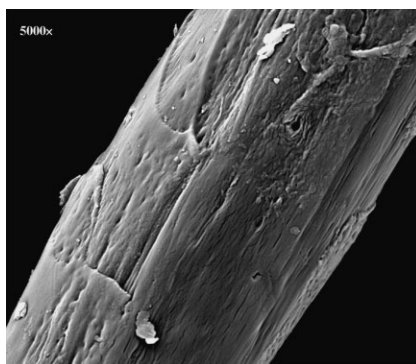


Figure 6.

Secondary electron image shows that the scales have been filled in.

since these electrons can emerge from regions further within the bulk compared to secondary electrons (Figure 6), which arise from the first 100 Angstroms of the surface. Combined, the SEM images suggest that the nanoparticle-modified keratin is capable of both filling in the scales, as we have seen for KP+Tgase, and creating a significant number of silver nanoparticle/keratin domains on the fabric surface.

UV-VIS analysis of the nanoparticle KP+mTgase treated fabric showed a weak and broad absorption band with a λ_{max} of approximately 424nm, as demonstrated in Figure 7. A weak absorption is consistent with visual examination of the fabrics, which reveals that treated fabrics do not appear to deviate in color from the original material, and with findings from SEM, confirming domains of silver nanoparticle density. While the fabric did not appear to have taken the color of the initial colloid,

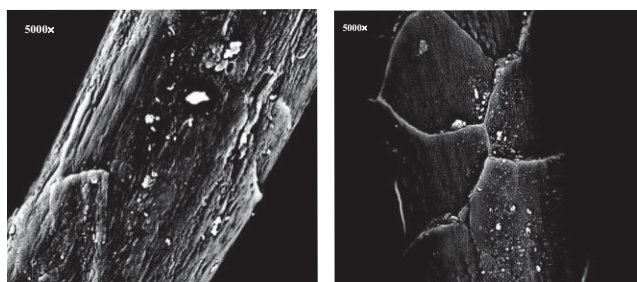


Figure 5.

Backscattered electron images showing silver nanoparticle deposits as bright spots.

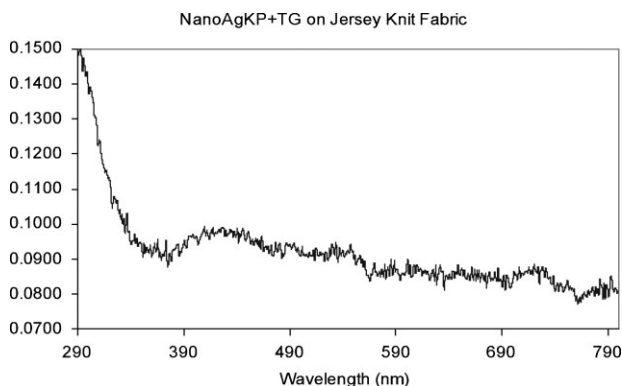


Figure 7.
UV-VIS of treated fabric.

we are excited about the possibilities of enzyme-mediated cross-linking as a tool for delivering nanoparticles to wool. The lack of color in these fabrics may make them easily compatible with existing dyes, while adjustment of the reaction conditions may ultimately produce colored textiles. Future work will examine the antibacterial efficacy of the fabrics prepared using this method.

Conclusion

We have clearly demonstrated that the combination of solubilized keratin and mTgase results in a fabric that resists shrinking and exhibits improved strength. This approach was extended to deliver silver nanoparticles to the wool fabric. TEM analysis was used to visualize high order polygonal silver nanoparticles formed from visible light irradiation. These nanoparticles were added in solution to keratin hydrolysate to produce a keratin hydrolysate material concentrated with silver nanoparticles. This material was used in the cross-linking reaction with mTgase to produce fabrics with a bound nanoparticle moiety that was found to be resistant to rinsing with agitation. This conclusion was supported by the appearance of strong contrast in the backscattered electron images, produced when electrons scatter

back from the sample as a function of the atomic number. Additionally, a weak absorbance band was identified using UV-VIS which was attributed to the surface plasmon band, an optical phenomenon found in metal nanoparticles. The low intensity of this band was consistent with visual inspection of the treated fabrics, which had not taken the color of the nanoparticle solution. Secondary electron images showed a smoothed scalar morphology, which is expected to maintain the beneficial shrink-proofing observed for KP+mTgase samples, but has not yet been tested. Combined, the data suggest that this approach offers a means to deliver nanoparticles while imparting shrink resistance. Future studies will investigate the treated fabrics for beneficial properties afforded by bound nanoparticles such as antibacterial efficacy, improved temperature performance, fiber strength, and shrink resistance. The results reported in this article are the subject of a patent application.

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